

## Aluminum dihydrogen tripolyphosphate:

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## Accepted Manuscript

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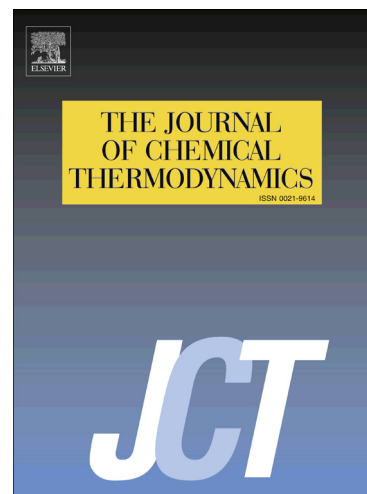
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**Aluminum dihydrogen tripolyphosphate: thermodynamic characteristics**

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**Abstract**

For the first time solution enthalpies of Al, H<sub>3</sub>PO<sub>4</sub>, and AlH<sub>2</sub>P<sub>3</sub>O<sub>10</sub> x 2H<sub>2</sub>O in 2 mol dm<sup>-3</sup> NaOH have been measured as following:  $\Delta_{\text{sol}}H^{\circ}_1 = -404.75 \pm 4.36 \text{ kJ mol}^{-1}$ ;  $\Delta_{\text{sol}}H^{\circ}_2 = -189.48 \pm 0.54 \text{ kJ mol}^{-1}$ ;  $\Delta_{\text{sol}}H^{\circ}_3 = -238.95 \pm 3.32 \text{ kJ mol}^{-1}$ . On the basis of experimental data the standard molar enthalpy of formation and enthalpies of some reactions with participation of AlH<sub>2</sub>P<sub>3</sub>O<sub>10</sub> x H<sub>2</sub>O were calculated. The enthalpy of interaction of Al with H<sub>3</sub>PO<sub>4</sub> is  $\Delta_rH^{\circ} = -734.24 \pm 5.56 \text{ kJ mol}^{-1}$ . It was established that according to thermodynamic data Al<sub>2</sub>O<sub>3</sub> can react with H<sub>3</sub>PO<sub>4</sub> forming investigated compound at 513 K. Employed compound (AlH<sub>2</sub>P<sub>3</sub>O<sub>10</sub> x H<sub>2</sub>O) can react with H<sub>2</sub>O with formation of AlPO<sub>4</sub> and phosphorous acid. All the data were obtained for the first time.

Keywords: aluminum dihydrogen tripolyphosphate; solution calorimetry; thermochemical characteristics; standard molar enthalpy of formation

**1. Introduction**

Layer materials with low-dimensional structure have wide set of unique properties such as ion exchange, ionic conductivity, intercalation, catalytic activity and other [1 -11]. For the reason the compounds are applied in different fields of technique. In papers [1, 3, 5, 8] the series of materials with composition M<sup>III</sup>H<sub>2</sub>P<sub>3</sub>O<sub>10</sub> x 2H<sub>2</sub>O (where M<sup>III</sup> =Al, Ga, Fe, Mn, V, Cr), which have layer structure, is examined. Aluminum dihydrogen tripolyphosphate which belongs to these classes of materials is already used as a new non-toxic white anticorrosive pigment for painting. For perspective application it is necessary to investigate physico-chemical properties of AlH<sub>2</sub>P<sub>3</sub>O<sub>10</sub> x 2H<sub>2</sub>O in detail. In paper [1] the structure of the compound was studied for the first

time. It was enough difficult to determine the structure of aluminum dihydrogen tripolyphosphate because it has complex structure.

To optimize processes of synthesis of above mentioned compound it is useful to know thermodynamic data. Thermodynamic characteristics allow one to predict interaction with different external reagents, for example, with water, to study compound stability, decomposition, etc. Consideration of literature papers showed that there are no data on thermodynamics of aluminum dihydrogen tripolyphosphate. In paper [8] the conductivity and stability of  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$  were studied. Authors [8] showed that in vapor water above mentioned compound transfer first of all in  $\text{Al}(\text{H}_2\text{PO}_4)_3$  and then in  $\text{AlPO}_4$ .

In our paper we for the first time investigated the thermodynamic properties of aluminum dihydrogen tripolyphosphate by solution calorimetry, namely, we measured solution enthalpy, standard molar enthalpy of formation and enthalpies of reactions. In future we plan to measure thermodynamic functions for compounds  $\text{M(III)H}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$  (M(III) is metal of third group) to construct dependence “thermodynamic property-structural property”. Knowledge of these relations is very important to understand the nature of properties change [12].

## 2. Experimental part

### *Synthesis and identification of sample*

We used sample of  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$  which was prepared and characterized in paper [1].  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$  was prepared from  $\text{H}_3\text{PO}_4$  and  $\text{Al}_2\text{O}_3$  [1]. Phosphorous acid and aluminum oxide was mixed in ratio 6:1 and heated up to 513 K ( $t = 24$  h). Then mixture was slowly cooled to room temperature during 48 h. Forming white microcrystalline product was washed with water. According to data [1] the sample has layer structure and the layers appear to be held together by a hydrogen bonding network, principally involving the presence of two water molecules per formula unit within the interlamellar region, which are each hydrogen bonded to the hydroxyl groups of the hydrogen triphosphate.

Identification of sample was performed by power X-ray diffraction [1]. Rietveld analysis was performed using the GSAS program. According to power data the compound  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$  has monoclinic structure (space group P2/c) with lattice parameters:  $a = 0.79381(3)$  nm,  $b = 0.49188(2)$  nm,  $c = 1.16286(4)$  nm,  $\beta = 95.739(2)^\circ$ ,  $V = 0.45178(4)$  nm<sup>3</sup>. Detailed information about structure is presented in paper [1].

Sample  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$  was characterized by chemical analysis as well. For the analysis of Al, P an atomic absorption method was used. CHN analyzer Evrovector 600 was used to determine H content. We used obtained sample, aluminium (>99%) and phosphorous acid (Aldrich, 85%) to perform calorimetric experiments. Detailed information is presented in Table 1.

#### *Thermochemical cycle*

We have chosen solution calorimetry as method of investigation to obtain thermochemical properties of aluminum dihydrogen tripolyphosphate. For this aim it was necessary to select solvent in such a way that  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$  and initial components are solved in solvent. We checked that  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$  was not solved in hydrochloric acid but solved in NaOH. To construct thermochemical cycle we tried to solve  $\text{Al}_2\text{O}_3$  in NaOH but it was impossible. So, we have chosen calorimetric cycle in such a way that Al and  $\text{H}_3\text{PO}_4$  are solved in NaOH. The schema is presented in Table 2.  $2 \text{ mol dm}^{-3}$  NaOH have been chosen to perform experiments.

All experiments with aluminum were performed in dry box. It was made to avoid interaction of aluminum with oxygen and air moisture. Dry box was filled by argon. The procedure was following. Aluminum tape (99.99%) was placed into dry box. Further aluminum was crushed by special way, preliminary weighed using balance located in dry box. Then aluminum was placed in weighed glass ampoules. After that ampoules were closed by special caps, took out from box and soldered. The weight of aluminum was determined as difference of empty ampoule and ampoule with substance.

After we choose NaOH as solvent it was necessary to select concentration of alkali. Concentration should be so that all substances were dissolved with enough speed for measurements. The investigated substance ( $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$ ) and phosphoric acid are dissolved in alkali (since  $1 \text{ mol dm}^{-3}$  concentration) very quickly (about 5 minutes). The crushed aluminum is dissolved since  $2 \text{ mol dm}^{-3}$  of alkali within 10 minutes. For this reason  $2 \text{ mol dm}^{-3}$  NaOH was selected as solvent.

#### *Experimental technique*

The enthalpies of solution were measured in the calorimeter that has been described in

papers [13-16]. The calorimeter was constructed as Dewar glass vessel (250 cm<sup>3</sup>) placed in a brass capsule. The calorimeter was closed hermetically by cover which made of brass and covered with teflon. The thermometer for measurement of calorimeter temperature, the device for broken and washing of calorimetric ampoules, the mixer for hashing of liquid placed in calorimeter, and the heater for carrying out calibration were placed on cover. Resistance of thermometer was measured by the precision voltmeter (Schlumberger firm) Solartron 7061. Power on the heater was given by means of the precision regulator of power. Voltage and current were measured by the second precision Solartron 7061 voltmeter. The device for broken of ampoules and the heater was symmetrized to avoid the errors connected with location of heat source and calibration source (see paper [17]).

The repeatability of calorimeter on heat equivalent was 0.03% (it is standard uncertainty). Dissolution of potassium chloride in water was performed to check operation of calorimeter. The obtained dissolution heat of KCl was  $17.41 \pm 0.08 \text{ kJ mol}^{-1}$  (the molality of the final solution was  $0.028 \text{ mol kg}^{-1}$ ,  $T = 298.15 \text{ K}$ ). The type of uncertainty presented by us for dissolution enthalpy of KCl is standard uncertainty. The literature data is:  $17.42 \pm 0.02 \text{ kJ mol}^{-1}$  [18]. As it is possible to see the value which we measured is in a good agreement with literature data.

## Results and discussion

Detail information on synthesis and identification of obtained compound is presented in paper [1]. Compound is individual phase with composition  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$ .

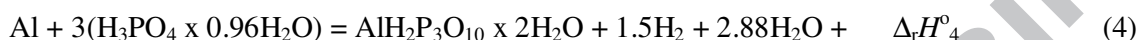
We measured the following solution enthalpies for Al,  $\text{H}_3\text{PO}_4$  (85%) and aluminum dihydrogen tripolyphosphate:  $\Delta_{\text{sol}}H^{\circ}_1 = -404.75 \pm 1.65 \text{ kJ mol}^{-1}$ ;  $\Delta_{\text{sol}}H^{\circ}_2 = -189.48 \pm 0.54 \text{ kJ mol}^{-1}$ ;  $\Delta_{\text{sol}}H^{\circ}_3 = -238.95 \pm 3.32 \text{ kJ mol}^{-1}$ .  $\Delta_{\text{sol}}H^{\circ}_2$  was calculated for mole of 85%  $\text{H}_3\text{PO}_4$  which equal to  $\text{H}_3\text{PO}_4 \times 0.96\text{H}_2\text{O}$ . Detail information is presented in Tables 3-5. The type of uncertainty presented by us here is standard uncertainty.

We used experimental data of paper [19] to understand how much  $\text{Al}_2\text{O}_3$  can be on the surface of Al. According to data [19] the degree of conversion of Al films with a thickness of 50 nm to  $\text{Al}_2\text{O}_3$  at treatment not higher than 523 K is less than 1%. In our experiments we used Al with a minimum thickness of 0.1 mm ( $10^5 \text{ nm}$ ). Thus, according to above mentioned data [19] the amount of  $\text{Al}_2\text{O}_3$  on the surface of Al which we used in our experiments is less than 1%.

On the basis of these data we increased the uncertainty for  $\Delta_{\text{sol}}H^{\circ}_1$ . The corrected value is:  $\Delta_{\text{sol}}H^{\circ}_1 = -404.75 \pm 4.36 \text{ kJ mol}^{-1}$ . Here it is necessary to mention the following. The value of

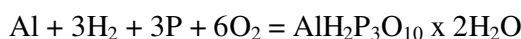
formation enthalpy for  $\text{NaAlO}_2$  measured in paper [20] is based on solution enthalpy of Al (aluminum) in HCl. This value is used in Reference Book [18]. Authors [20] did not use dry box for procedures with Al. Authors [20] also did not increase the uncertainty for solution enthalpy of Al which can be connected that  $\text{Al}_2\text{O}_3$  surface layers on Al samples were not removed prior to the experiments.

On the basis of experimental values  $\Delta_{\text{sol}}H^{\circ}_1$ ,  $\Delta_{\text{sol}}H^{\circ}_2$ ,  $\Delta_{\text{sol}}H^{\circ}_3$  we calculated the enthalpy of reaction:



$$\Delta_r H^{\circ}_4 = -734.24 \pm 5.56 \text{ kJ mol}^{-1}$$

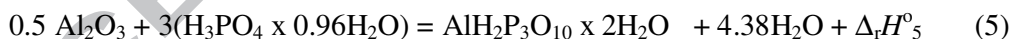
On the basis of standard molar enthalpies of formation of phosphorous acid (85%) and water we calculated the standard molar enthalpy of formation of  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$  as following:



$$\Delta_f H^{\circ} (298.15, \text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}) = -3734.64 \pm 5.97 \text{ kJ mol}^{-1}.$$

Then, it is interesting to calculate the reaction enthalpy of formation of investigated compound from aluminum oxide and phosphorous acid because  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$  is prepared from  $\text{H}_3\text{PO}_4$  and  $\text{Al}_2\text{O}_3$  at 513 K.

We used formation enthalpy of reaction (4), formation enthalpy for  $\text{Al}_2\text{O}_3$  and  $\text{H}_2\text{O}$  [18] to calculate the enthalpy of reaction:



Obtained value of reaction enthalpy is following:

$$\Delta_r H^{\circ}_5 (298.15 \text{ K}) = -325.13 \pm 5.63 \text{ kJ mol}^{-1}.$$

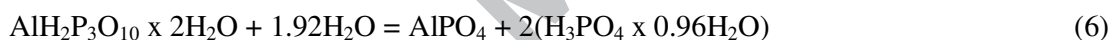
As it is possible to see the reaction enthalpy is negative value. To understand whether reaction takes place it is necessary to know Gibbs free energy:  $\Delta G = \Delta H - T \Delta S$ . To calculate Gibbs free energy it is necessary to know entropies of all compounds employed in reaction (5). Entropies of  $\text{Al}_2\text{O}_3$  and  $\text{H}_2\text{O}$  were taken from reference book [18], entropy of phosphorous acid

was taken from paper [21], and entropy of investigate compound were estimated by us using data on entropies of  $\text{Al}_2\text{O}_3$ ,  $\text{H}_2\text{O}$  and  $\text{P}_4\text{O}_{10}$ . Then we calculate the free Gibbs energy for above reaction at 513 K as following:

$$\Delta_r G_5^{\circ}(513 \text{ K}) = -402.54 \pm 5.81 \text{ kJ mol}^{-1}$$

The value is negative. It means that reaction of formation of our compound from aluminum oxide and phosphorous acid is thermodynamically favorable. It is observed in practice. As was mentioned the synthesis of  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$  was performed from  $\text{Al}_2\text{O}_3$  and  $\text{H}_3\text{PO}_4$  at 513 K.

Then it is interesting to calculate the thermodynamic characteristics of reaction of  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$  interaction with water because there are data in paper [9] that compound reacts with water decomposed on  $\text{Al}(\text{H}_2\text{PO}_4)_3$  and  $\text{H}_3\text{PO}_4$  and then on  $\text{AlPO}_4$  and  $\text{H}_3\text{PO}_4$ . We could not find thermodynamic data for compound  $\text{Al}(\text{H}_2\text{PO}_4)_3$  in literature. We found only data for compound  $\text{AlPO}_4$  in reference book [18]. So, we calculated thermodynamic data for reaction:



To calculate enthalpy of reaction (6) we used standard molar enthalpy of formation of  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$  obtained by us. We also took standard molar enthalpies of formation of aluminum phosphate, water and phosphorous acid from reference book [18].

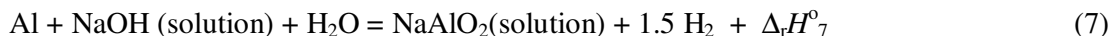
Then we calculated the Gibbs free energy at 423 K using entropy of  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$  estimated by us, entropies of water,  $\text{AlPO}_4$  and phosphorous acid taken from references [18, 21]. The obtained value is:

$$\Delta_r G_6^{\circ} = -25.75 \pm 5.32 \text{ kJ mol}^{-1}.$$

As we can see the Gibbs free energy is negative value. So, it is possible to conclude that according to thermodynamic data the investigated compound can react with water. It confirmed information of paper [8] that  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$  decomposed to  $\text{AlPO}_4$  and phosphorous acid at 423 K.

Using thermochemical data from reference book [18] we calculated the enthalpy for reaction of Al interaction with NaOH:





$$\Delta_r H^\circ_7 = -419.07 \pm 1.56 \text{ kJ mol}^{-1}$$

We would like to compare this value with value of aluminum in NaOH obtained by us. Preliminary it is necessary to say the following. It is not known exactly if NaAlO<sub>2</sub> or other compound is formed after solution of Al in NaOH. So, the comparison performed by us here is not exact but useful. From experimental data the solution enthalpy of Al obtained by us is  $\Delta_{\text{sol}} H^\circ_1 = -404.75 \pm 1.65 \text{ kJ/mol}$ . Then we increased the uncertainty which can be connected with possibility of Al<sub>2</sub>O<sub>3</sub> layers on the surface of Al. The obtained value is:  $\Delta_{\text{sol}} H^\circ_1 = -404.75 \pm 4.36 \text{ kJ mol}^{-1}$ . We carefully considered the data of papers [20] and [22] on which the formation enthalpy for NaAlO<sub>2</sub> was based. It is possible to say following. In paper [20] the formation enthalpy for NaAlO<sub>2</sub> was obtained on the basis of solution enthalpy of aluminum in HCl at 303.15 K. Authors [20] did not indicate the type of uncertainty. Authors [20] also did not add uncertainty which can be connected with present of Al<sub>2</sub>O<sub>3</sub> on surface of Al. They did not perform experiments with Al in dry box. There is no uncertainty connected with recalculation of formation enthalpy for NaAlO<sub>2</sub> from 303.15 K up to 298.15 K. Authors [22] performed calorimetric experiments at 975 K and did not add uncertainty connected with recalculation of formation enthalpy for NaAlO<sub>2</sub> from 975 K up to 298.15 K. According our opinion, it is necessary to increase uncertainty for reaction (7) up to 1.5% or more. After increasing uncertainty the value for reaction (7) is  $\Delta_r H^\circ_7 = -419.07 \pm 8.07 \text{ kJ mol}^{-1}$  but our value is  $-404.75 \pm 4.36 \text{ kJ mol}^{-1}$ . It is also necessary to mention that formation enthalpy for NaAlO<sub>2</sub> in Reference Book [18] is differing from the same value in Canadian database FACT [22]. If criteria 3 $\sigma$  for uncertainty is used that confidence intervals are crossed. It is necessary to mention once more that this comparison is not exact but useful.

## Conclusion

We created thermochemical cycle to determine the standard molar enthalpy of formation of AlH<sub>2</sub>P<sub>3</sub>O<sub>10</sub> x 2H<sub>2</sub>O. Cycle was constructed in such a way that investigated compound solved in 2 mol dm<sup>-3</sup> NaOH and solution enthalpy was compared with solution enthalpy of Al and phosphorous acid. We measured solution enthalpy of AlH<sub>2</sub>P<sub>3</sub>O<sub>10</sub> x 2H<sub>2</sub>O for the first time. On

the basis of experimental data the standard molar enthalpy of formation and enthalpies of some reactions with participation of  $\text{AlH}_2\text{P}_3\text{O}_{10} \times \text{H}_2\text{O}$  were calculated. It was established that according to thermodynamic data  $\text{Al}_2\text{O}_3$  reacts with  $\text{H}_3\text{PO}_4$  forming investigated compound at 513 K. Employed compound ( $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$ ) reacts with  $\text{H}_2\text{O}$  with formation of  $\text{AlPO}_4$  and phosphorous acid. All the data were obtained for the first time.

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TABLE 1

Characterization of chemical samples used in this study

| Chemical name                        | Chemical formula   | Source                 | State  | Mass fraction purity |
|--------------------------------------|--|------------------------|--------|----------------------|
| Aluminum dihydrogen tripolyphosphate | $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$ | Synthesis              | Solid  | >0.99                |
| Phosphorous acid (85wt. %)           | $\text{H}_3\text{PO}_4 \times 0.96\text{H}_2\text{O}$            | Aldrich                | Liquid | >0.998               |
| Aluminum                             | Al   | Bolkan Eco Trader Ltd. | Solid  | >0.99                |
| Sodium hydroxide                     | NaOH   | Aldrich                | Solid  | >0.99                |

The following methods of analysis were used.  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$ : atomic absorption method and CHN analysis;  $\text{H}_3\text{PO}_4 \times 0.96\text{H}_2\text{O}$ : atomic absorption method and CHN analysis; Al: atomic absorption and mass-spectrometry methods; NaOH: atomic absorption method and CHN analysis.

Atomic absorption method: spectrometer iCE3000; ways of atomization: flame, graphite furnace; methods of supply: aerosol; calibration by standard solutions; the standard uncertainty is 0.1-0.5%.

Mass-spectrometry method: EMAL-2 laser ionization mass spectrometer ( $F = 10\text{-}100$  hertz,  $E = 1\text{-}10$  MJ); detection limits:  $10^{-4}\text{-}10^{-6}$  mass.%;  $F$ - frequency,  $E$  – energy.

CHN analysis: analyzer Evrovector 600; standard Deviations: C – 0.065; H -0.050.

TABLE 2

Reaction scheme for the formation enthalpy of  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2 \text{H}_2\text{O}$  from Al and  $\text{H}_3\text{PO}_4 \times 0.96\text{H}_2\text{O}$  at the temperature 298.15 K and pressure  $p = 0.1 \text{ MPa}$ .  $\Delta_r H_4^\circ = \Delta_{\text{sol}} H_1^\circ + 3\Delta_{\text{sol}} H_2^\circ - \Delta_{\text{sol}} H_3^\circ$ . Solution 1 is  $2 \text{ mol dm}^{-3} \text{ NaOH}^a$ .

| Nr | Reaction   | $\Delta_r H_m^\circ / \text{kJ mol}^{-1}$ |
|----|--|---|
| 1  | $\text{Al} + \text{solution 1} = \text{solution 2} + 1.5\text{H}_2$  | $\Delta_{\text{sol}} H_1^\circ$           |
| 2  | $3(\text{H}_3\text{PO}_4 \times 0.96\text{H}_2\text{O}) + \text{solution 2} = \text{solution 3} + 2.88\text{H}_2\text{O}$  | $3\Delta_{\text{sol}} H_2^\circ$          |
| 3  | $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2 \text{H}_2\text{O} + \text{solution 1} = \text{solution 3}$  | $\Delta_{\text{sol}} H_3^\circ$           |
| 4  | $\text{Al} + 3(\text{H}_3\text{PO}_4 \times 0.96\text{H}_2\text{O}) = \text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O} + 1.5\text{H}_2 + 2.88\text{H}_2\text{O}$ | $\Delta_r H_4^\circ$                      |

<sup>a</sup>Standard uncertainties  $u$  are  $u(T) = 0.01 \text{ K}$ ,  $u(p) = 0.05p$ ,  $u(c_{\text{NaOH}}) = 0.003 \text{ mol dm}^{-3}$

TABLE 3

The molar solution enthalpies ( $\Delta_{\text{sol}}H^0$ ) of mass ( $m$ ) of Al (molar mass: 26.98 g mol<sup>-1</sup>) in 250 cm<sup>3</sup> of 2 mol dm<sup>-3</sup> NaOH at the temperature 298.15 K and pressure  $p = 0.1$  MPa<sup>a</sup>

| $m/\text{g}$ | $H_e/\text{J } \Omega^{-1}$ | $H/\text{J g}^{-1}$ | $\Delta_{\text{sol}}H^0/\text{kJ mol}^{-1}$ |
|--------------|-----------------------------|---------------------|---|
| 0.010675     | 2.1149                      | -14930              | -402.85                                     |
| 0.010317     | 2.0444                      | -14811              | -399.65                                     |
| 0.010210     | 2.1554                      | -15176              | -409.49                                     |
| 0.010685     | 1.94430                     | -15042              | -405.86                                     |
| 0.011064     | 2.20488                     | -15043              | -405.88                                     |

Here:  $H_e$  is heat equivalent,  $H$  is enthalpy, the standard uncertainty is provided. <sup>a</sup>Standard uncertainties  $u$  are  $u(T) = 0.01$  K,  $u(p) = 0.05p$ ,  $u(m) = 0.000005$  g,  $u(c_{\text{NaOH}}) = 0.003$  mol dm<sup>-3</sup>,  $u(H_e) = 0.0001$  J  $\Omega^{-1}$ ,  $u(H) = 61$  J g<sup>-1</sup>,  $u(V) = 0.003$  dm<sup>-3</sup>,  $u(\Delta_{\text{sol}}H^0) = 1.65$  kJ mol<sup>-1</sup>

TABLE 4

The molar solution enthalpies ( $\Delta_{\text{sol}}H^0$ ) of mass ( $m$ ) of  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$  (molar mass: 317.94 g  $\text{mol}^{-1}$ ) in 250  $\text{cm}^3$  of 2  $\text{mol dm}^{-3}$  NaOH at the temperature 298.15 K and pressure  $p = 0.1 \text{ MPa}^a$ .

| $m/\text{g}$ | $H_e/\text{J } \Omega^{-1}$ | $H/\text{J g}^{-1}$ | $\Delta_{\text{sol}}H^0/\text{kJ mol}^{-1}$ |
|--------------|-----------------------------|---------------------|---|
| 0.124887     | 2.0855                      | -750.84             | -238.72                                     |
| 0.210535     | 2.0332                      | -750.47             | -238.61                                     |
| 0.162898     | 2.0339                      | -769.64             | -244.70                                     |
| 0.162898     | 2.0029                      | -753.21             | -239.48                                     |
| 0.144941     | 2.0131                      | -733.52             | -233.22                                     |

Here:  $H_e$  is heat equivalent,  $H$  is enthalpy, the standard uncertainty is provided. "Standard uncertainties  $u$  are  $u(T) = 0.01 \text{ K}$ ,  $u(p) = 0.05p$ ,  $u(m) = 0.000005 \text{ g}$ ,  $u(c_{\text{NaOH}}) = 0.003 \text{ mol dm}^{-3}$ ,  $u(H_e) = 0.0001 \text{ J } \Omega^{-1}$ ,  $u(H) = 10.44 \text{ J g}^{-1}$ ,  $u(V) = 0.003 \text{ dm}^{-3}$ ,  $u(\Delta_{\text{sol}}H^0) = 3.32 \text{ kJ mol}^{-1}$

TABLE 5

The molar solution enthalpies ( $\Delta_{\text{sol}}H^0$ ) of mass ( $m$ ) of  $\text{H}_3\text{PO}_4 \times 0.96\text{H}_2\text{O}$  (molar mass: 115.29 g  $\text{mol}^{-1}$ ) in 250  $\text{cm}^3$  of solution 2\* at the temperature 298.15 K and pressure  $p = 0.1 \text{ MPa}^a$ .

| $m/\text{g}$ | $H_e/\text{J } \Omega^{-1}$ | $H/\text{J g}^{-1}$ | $\Delta_{\text{sol}}H^0/\text{kJ mol}^{-1}$ |
|--------------|-----------------------------|---------------------|---|
| 0.068179     | 2.0662                      | -1642.1             | -189.32                                     |
| 0.047984     | 2.0787                      | -1660.5             | -191.44                                     |
| 0.035920     | 1.9568                      | -1623.0             | -187.12                                     |
| 0.064793     | 2.2273                      | -1654.5             | -190.75                                     |
| 0.068166     | 2.0670                      | -1631.9             | -188.14                                     |
| 0.052597     | 2.1366                      | -1637.1             | -188.74                                     |
| 0.052004     | 2.1438                      | -1664.6             | -191.91                                     |
| 0.054585     | 2.0099                      | -1650.1             | -190.24                                     |
| 0.054561     | 2.2302                      | -1657.9             | -191.14                                     |
| 0.049324     | 1.9923                      | -1640.1             | -189.09                                     |
| 0.053143     | 2.1596                      | -1616.7             | -186.39                                     |

Here:  $H_e$  is heat equivalent;  $H$  is enthalpy; the standard uncertainty is provided; solution 2 is solution which was obtained after solution of 0.011 g Al ( $4 \times 10^{-4} \text{ mol Al}$ ) in 250  $\text{cm}^3$  of 2  $\text{mol dm}^{-3}$  NaOH. <sup>a</sup>Standard uncertainties  $u$  are  $u(T) = 0.01 \text{ K}$ ,  $u(p) = 0.05p$ ,  $u(m) = 0.000005 \text{ g}$ ,  $u(c_{\text{NaOH}}) = 0.003 \text{ mol dm}^{-3}$ ,  $u(H_e) = 0.0001 \text{ J } \Omega^{-1}$ ,  $u(H) = 4.7 \text{ J g}^{-1}$ ,  $u(V) = 0.003 \text{ dm}^{-3}$ ,  $u(\Delta_{\text{sol}}H^0) = 0.54 \text{ kJ mol}^{-1}$



Solution enthalpy of Al in  $2 \text{ mol dm}^{-3}$  NaOH was measured.

Solution enthalpy of  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$  in  $2 \text{ mol dm}^{-3}$  NaOH was measured.

The standard formation enthalpy of  $\text{AlH}_2\text{P}_3\text{O}_{10} \times 2\text{H}_2\text{O}$  was determined.

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